

CLAIMS

1. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by
5 comprising the steps of:

obtaining a sulfonic acid derivative by allowing an alkoxy silane compound having an amino group to react with a cyclic sultone; and

subjecting the sulfonic acid derivative to a condensation
10 reaction.

2. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing a
15 secondary or tertiary amine derivative which is obtained by allowing an alkoxy silane compound having an amino group to react with a compound having at least 2 epoxy groups in a molecule to react with a cyclic sultone; and

subjecting the sulfonic acid derivative to a condensation
20 reaction.

3. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing a
25 secondary or tertiary amine derivative which is obtained by

allowing an alkoxy silane compound having an epoxy group to react with an amine compound having at least 2 amine valences (number of hydrogen atoms originated in an amino group contained in one molecule) to react with a cyclic sultone; and

5 subjecting the sulfonic acid derivative to a condensation reaction.

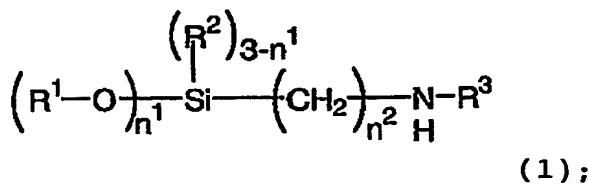
4. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

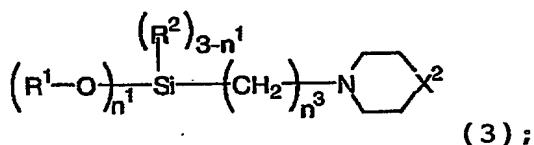
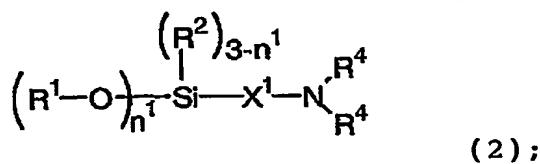
10 obtaining a sulfonic acid derivative by allowing a secondary or tertiary amine derivative which is obtained by allowing an alkoxy silane compound having an amino group to react with an alkoxy silane compound having an epoxy group to react with a cyclic sultone; and

15 subjecting the sulfonic acid derivative to a condensation reaction.

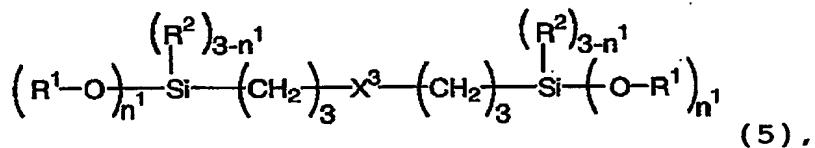
5. The production method as set forth in Claim 1, 2 or 4, wherein the alkoxy silane compound having an amino group is represented by the following general formulae (1) to (5):

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$$5 \quad (\text{R}^1\text{-O})_3\text{-Si-R}^5 \quad (4); \text{ and}$$



wherein R¹ represents a methyl group or an ethyl group;

10 R² represents a hydrogen atom, a methyl group or an ethyl group;

R^3 represents a hydrogen atom, a methyl group, an ethyl group, an allyl group, a phenyl group or an organic group represented by the following general formula (6);

15 R⁴ represents a methyl group, an ethyl group or a hydroxyethyl group;

R^5 represents a 3-(N-phenylamino)propyl group, a 3-(4,5-dihydroimidazolyl)propyl group or a 2-[N-(2-aminoethyl)aminomethyl phenyl]ethyl group;

x^1 represents a divalent alkylene having from 1 to 6 carbon atoms;

x^2 represents methylene which is a divalent organic group, oxygen or a secondary amine;

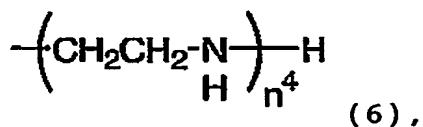
5 x^3 represents a divalent organic group represented by -NH- or -NHCH₂CH₂NH-;

n^1 represents an integer of from 1 to 3;

n^2 represents an integer of from 1 to 6; and

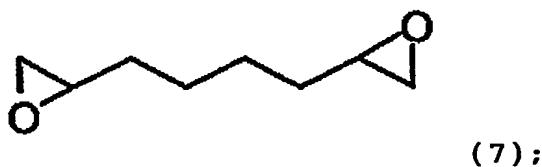
n^3 represents an integer of from 1 to 3:

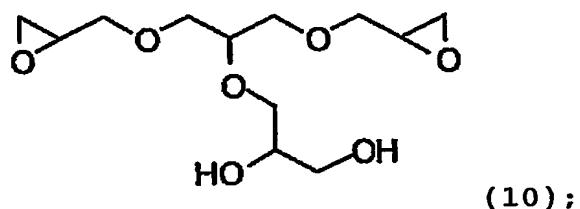
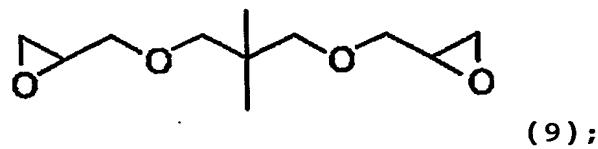
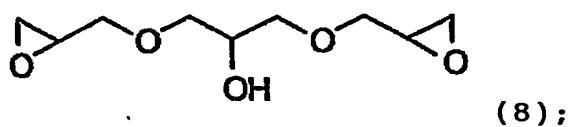
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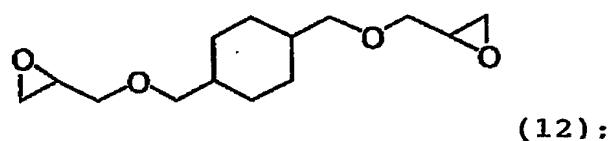
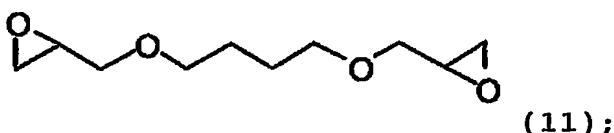
wherein n^4 represents an integer of from 0 to 2.

6. The production method as set forth in Claim 2, wherein
15 the compound having at least 2 epoxy groups in a molecule is
represented by the following general formulae (7) to (28):

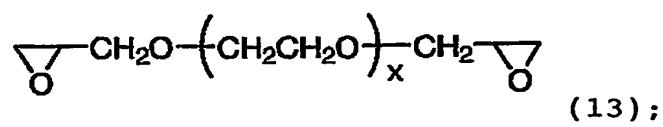


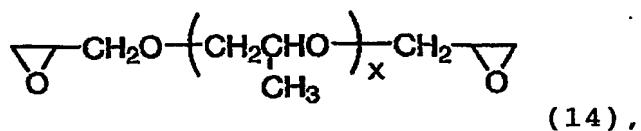


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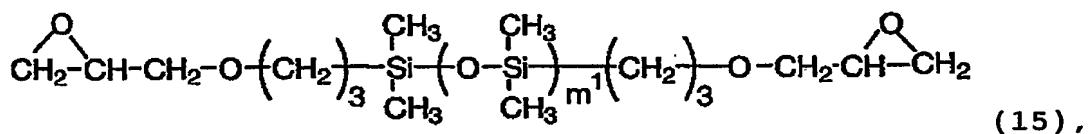


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wherein x represents an integer of from 1 to 1000;

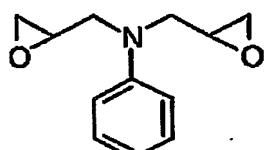


wherein m^1 represents an integer of from 1 to 100;

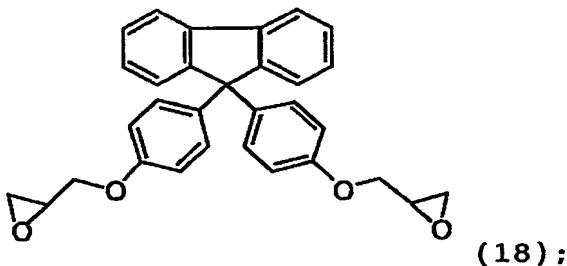


(16);

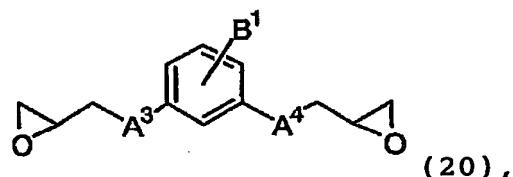
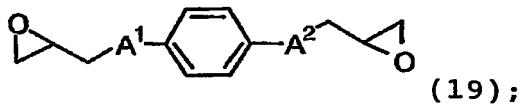
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(17);



(18);

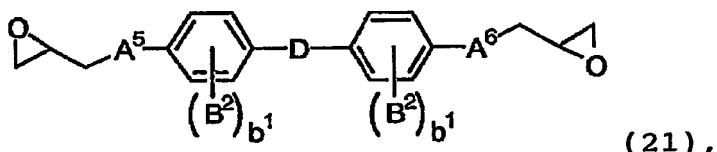


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wherein A^1 , A^2 , A^3 and A^4 each independently represents a divalent linking group selected from among $-O-$, $-C(=O)O-$, $-NHC(=O)O-$ and $-OC(=O)O-$; and

B^1 represents any one of substituents: $-H$, $-CH_3$ and $-OCH_3$;

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wherein A^5 and A^6 each independently represent a divalent linking group selected from among $-O-$, $-C(=O)O-$, $-NHC(=O)O-$ and $-OC(=O)O-$;

B^2 represents any one of substituents: $-H$, $-CH_3$ and $-OCH_3$;

b^1 represents an integer of from 0 to 4;

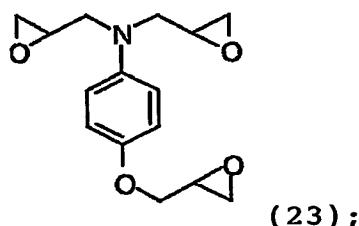
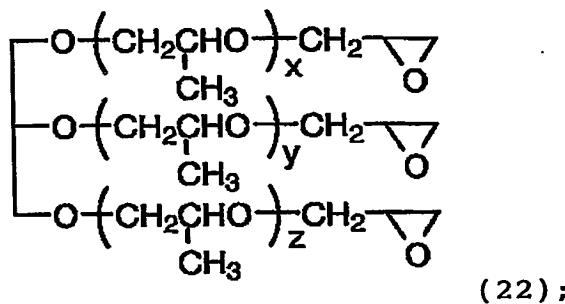
D represents a single bond or any one of divalent linking groups: $-O-$, $-C(=O)-$, $-C(=O)O-$, $-NHC(=O)-$, $-NH-$, $-N=N-$, $-CH=N-$, $-CH=CH-$, $-C(CN)=N-$, $-C\equiv C-$, $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,

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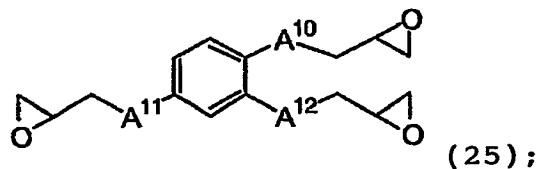
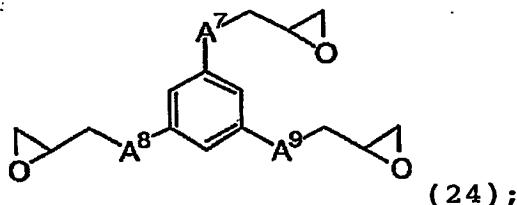
$-C(CH_3)_2-$ and the general formulae: $-O-(CH_2)_m-O-$ and $-O-(CH_2CH_2O)_n-$,

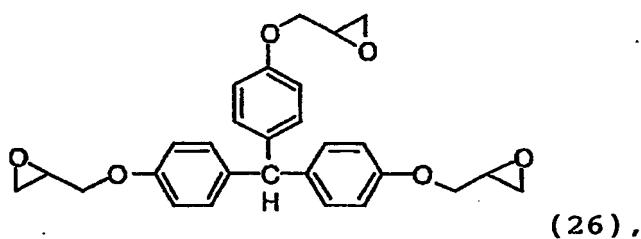
wherein m represents an integer of from 2 to 12; and
 n represents an integer of from 1 to 5;

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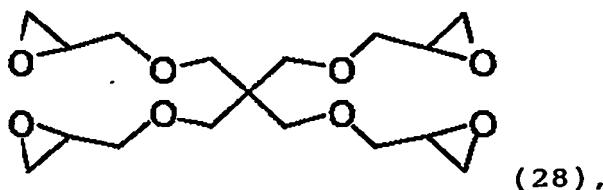
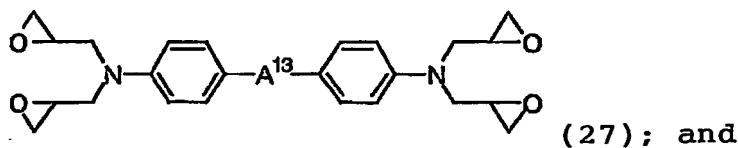




wherein x , y and z each independently represent an integer of from 1 to 20;

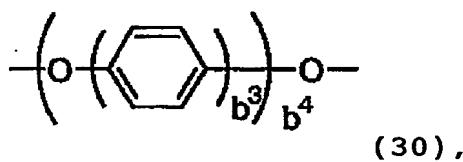
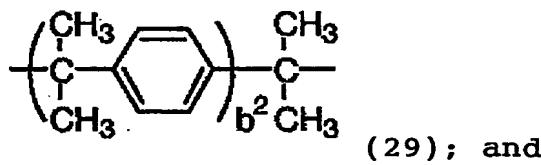
5 A^7 , A^8 and A^9 each independently represents a divalent linking group selected from among $-O-$, $-C(=O)O-$, $-NHC(=O)O-$, and $-OC(=O)O-$; and

10 A^{10} , A^{11} and A^{12} each independently represents a divalent linking group selected from among $-O-$, $-C(=O)O-$, $-NHC(=O)O-$ 10 and $-OC(=O)O-$;



wherein A^{13} represents methylene or a linking group represented by any one of the following general formulae (29)

and (30):



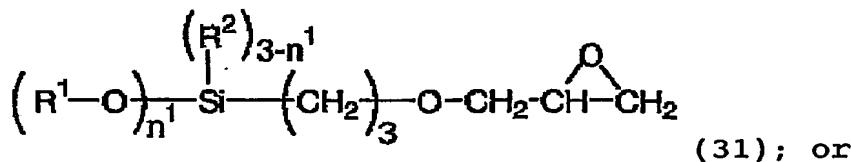
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wherein b^2 represents an integer of from 0 to 4;

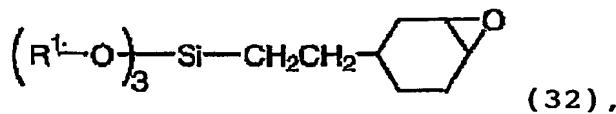
b^3 represents an integer of from 1 to 3; and

b^4 represents an integer of from 0 to 2.

10 7. The production method as set forth in Claim 3 or 4,
wherein the alkoxy silane compound having an epoxy group is
represented by the following general formula (31) or (32):



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wherein R^1 and R^2 each independently represents a methyl

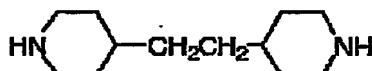
group or an ethyl group; and

n^1 represents an integer of from 1 to 3.

8. The production method as set forth in Claim 3, wherein the amine compound having at least 2 amine valences is
5 represented by the following general formulae (33) to (51):

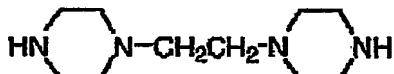


(33);

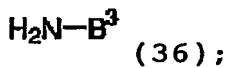


(34);

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(35);



(36);

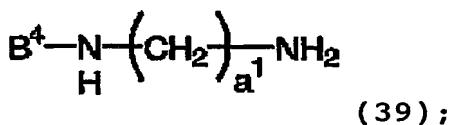
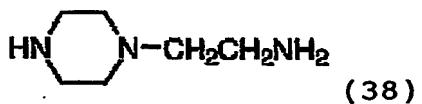
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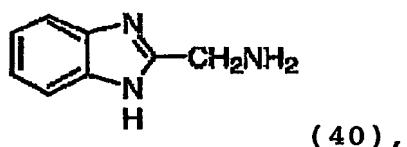
(37),

wherein B^3 represents a hydrocarbon group having from 2 to 18 carbon atoms or a group having at least one ether bond

in a hydrocarbon chain;

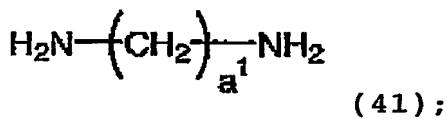


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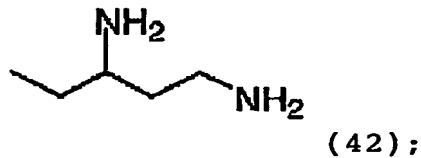


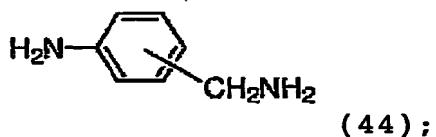
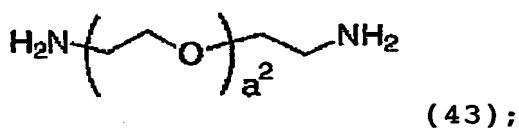
wherein a^1 represents an integer of from 2 to 18;

10 B^4 represents a hydrocarbon group having from 1 to 18 carbon atoms or a group having at least one ether bond in a hydrocarbon chain;

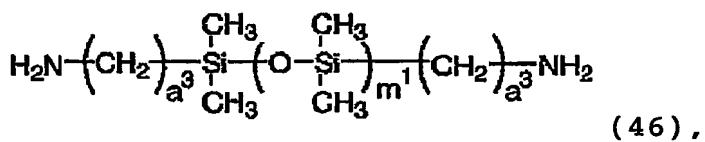
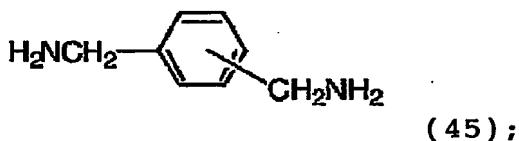


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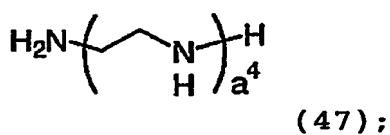


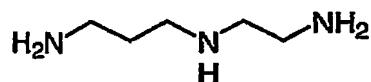
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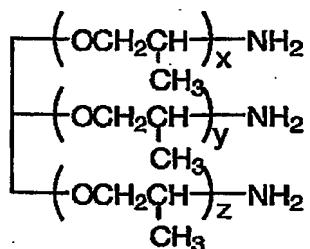
10 wherein a^1 represents an integer of from 2 to 18;
 a^2 represents an integer of from 1 to 10000;
 m^1 represents an integer of from 1 to 100; and
 a^3 represents an integer of from 3 to 18;

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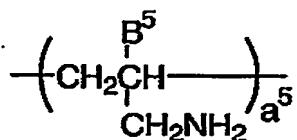


(48);

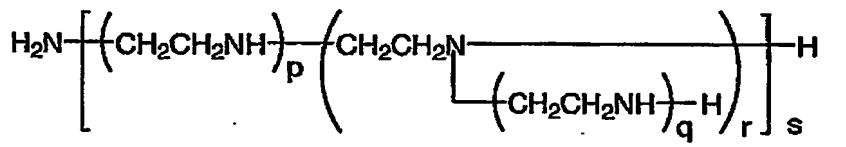


(49);

5



(50); and



(51),

10 wherein a^4 represents an integer of from 2 to 100;
 x, y and z each independently represents an integer of
 from 1 to 20;
 a^5 represents an integer of from 2 to 1000;
 B^5 represents hydrogen or a methyl group; and

p, q, r and s each independently represents an integer of from 1 to 20.

9. The production method as set forth in any one of Claims 1 to 8, wherein the cyclic sultone is represented by the following general formula (52) or (53):



(52); or



(53).

10 10. The production method as set forth in any one of Claims 1 to 9, being characterized in that a condensation reaction of an alkoxy silane portion of the sulfonic acid derivative is progressed by a catalytic action of an self-sulfonic acid group of the sulfonic acid derivative 15 generated by allowing to react with a cyclic sultone.

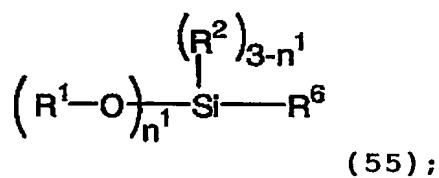
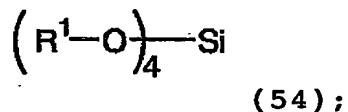
11. The production method as set forth in any one of Claims 1 to 10, being characterized in that the step for obtaining the sulfonic acid derivative and the condensation reaction step are simultaneously progressed.

20 12. The production method as set forth in any one of Claims 1 to 11, being characterized in that the condensation reaction step is performed in the presence of a metal alkoxide

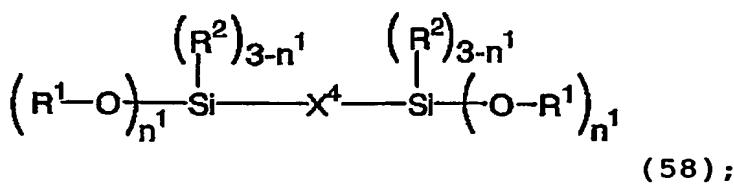
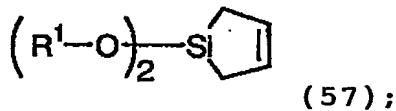
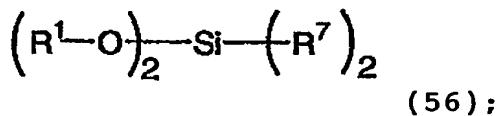
having no reactivity with an epoxy group and an amino group.

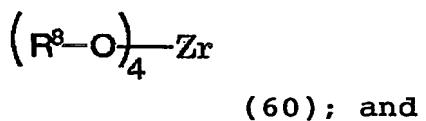
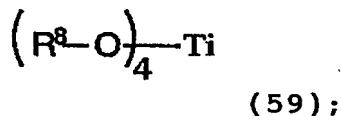
13. The production method as set forth in Claim 12, wherein the metal alkoxide is represented by the following general formulae (54) to (61):

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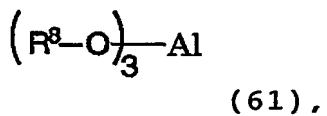


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wherein R¹ and R² each independently represents a methyl group or an ethyl group;

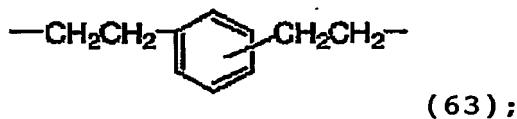
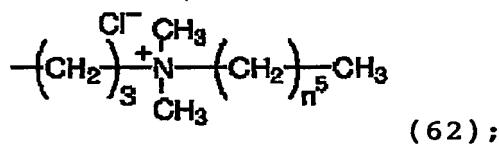
R⁶ represents an alkyl group or alkenyl group having from 10 1 to 18 carbon atoms, a 2-cyanoethyl group, a 3-cyanopropyl group, a cyclohexyl group, a 2-(3-cyclohexenyl)ethyl group, a 3-cyclopentadienyl propyl group, a phenyl group, a toluyl group or a monovalent organic group having a quaternary ammonium 15 group represented by the following general formula (62);

R⁷ represents a cycloalkyl group or cycloalkenyl group having 5 or 6 carbon atoms;

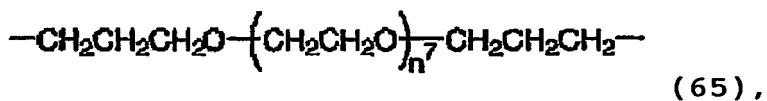
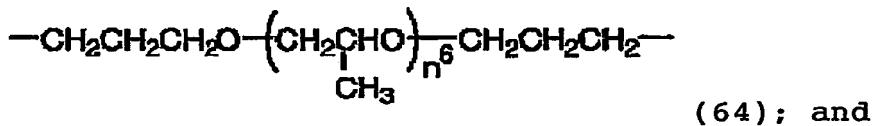
R⁸ represents an alkyl group or alkenyl group having from 1 to 4 carbon atoms;

X^4 represents a single bond, oxygen, an alkylene group having from 1 to 9 carbon atoms, a vinylene group or a divalent organic group represented by the following general formula (63) to (65); and

5 n^1 represents an integer of from 1 to 3:



10



15 wherein n^5 represents an integer of from 0 to 13; n^6 represents an integer of from 1 to 10; and n^7 represents an integer of from 0 to 20.

14. The production method as set forth in any one of

Claims 1 to 13, being characterized in that the condensation reaction step is performed in the presence of a metal oxide.

15. The production method as set forth in any one of Claims 1 to 14, being characterized in that the condensation reaction step is performed in the presence of an acid or an alkali.

16. The production method as set forth in any one of Claims 1 to 15, wherein the condensation reaction step is performed in an atmosphere of steam, an acidic or basic gas, and/or under a reduced pressure.

10 17. An organic-silica complex membrane, being obtained by the production method as set forth in any one of Claims 1 to 16.

18. A production method for an organic-silica complex membrane having a free sulfonic acid group in the complex membrane, being characterized in that the complex membrane as set forth in Claims 17 is dipped in a solvent containing an inorganic acid and/or an organic acid.

19. A production method for an organic-silica complex membrane having a free sulfonic acid group in the complex membrane, being characterized in that the complex membrane as set forth in Claim 17 is dipped in a solvent containing at least one type selected from the group consisting of: methyl sulfate, dimethyl sulfate, an alkyl halide having from 1 to 10 carbon atoms and an allyl halide having from 1 to 10 carbon atoms.

20. An organic-silica complex membrane, being obtained by the production method as set forth in Claim 18 or 19.

21. An electrolyte membrane, being characterized by comprising the organic-silica complex membrane as set forth 5 in Claim 17 or 20.

22. An electrolyte membrane, being obtained by dipping the organic-silica complex membrane as set forth in Claim 17 or 20 in a solvent containing a lithium ion.

23. An electrochemical device, being characterized by 10 comprising the electrolyte membrane as set forth in Claim 21 or 22.

24. A membrane transfer device, being characterized by comprising the organic-silica complex membrane as set forth in Claim 17 or 20.

15 25. A membrane reaction device, being characterized by comprising the organic-silica complex membrane as set forth in Claim 17 or 20.